Prediction of thermal conductivities of oxygen, nitrogen and carbon dioxide at the moderate density regime via semi-empirical assessment

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Abstract−Thermal conductivities coefficients for gaseous state of N_2, O_2 and CO_2 at zero density are determined by the inversion technique. The Lennard-Jones 12-6 (LJ 12-6) potential energy function is used as the initial model potential required by the technique. The Wang Chang-Uhlenbeck-de Boer (WCUB) approach of the kinetic theory of gases has been used for calculating the contribution of molecular degree of freedom to the thermal conductivity of N_2, O_2 and CO_2. Also, the initial density dependence of gaseous thermal conductivity according to the Rainwater-Friend theory, which was given by Najafi et al., has been considered for N_2, O_2 and CO_2.

Key words: Kinetic Theory of Gases, Initial Density Dependence, Thermal Conductivity, Molecular Degree of Freedom, Interaction Potential, Collision Integrals, Direct Inversion Method

INTRODUCTION

Thermodynamics deals with the general principles and laws that govern the behavior of matter and with the relationships between material properties. The origins of these laws and quantitative values for the properties are provided by statistical mechanics, which analyses the interaction of molecules and provides a detailed description of their behavior. A macroscopic theory of thermodynamics, either reversible or irreversible, is useful on its own for a large class of physical problems we encounter in daily life and natural phenomena in general.

Thermodynamics applies to all types of systems in microscopic [Hill, 1960] or macroscopic aggregation [Kirkwood and Oppenhiem, 1960] and also provides a theoretical framework for correlating the equilibrium properties of any system.

Meanwhile, a newly emerging field of irreversible thermodynamics, in which linear irreversible thermodynamics are extended to the nonlinear regime and macroscopic phenomena far removed from equilibrium has ambiguity and non-uniqueness [Hwang, 2005].

The thermodynamic properties of fluids are of continuing interest for theoretical [Kwon et al., 1997, 2005; Jang et al., 2003; Oh, 2004, 2005; Oh and Park, 2005] and industrial applications [Park and Gemhling, 1995; Park and Lee, 1995; Kang et al., 1995]. The urgent demand of industry for accurate values and estimation schemes of thermodynamic properties [Oh, 2004, 2005; Oh and Park, 2005] is increasing, because working fluids are often mixtures. The need for sufficient data to reliably estimate thermodynamic properties of mixtures remains today a major industrial problem. Measurements are costly and time consuming. Thermodynamic properties often determine the feasibility of a process. Transport properties determine how large the equipment should be or the time scale of the operation. Transport properties play an important role in many natural and technical processes. There are three transport properties of great concern: diffusion, viscosity and thermal conductivity. Nowadays, a large body of research [Bae et al., 1994a, b; Kang and Sangani, 2002] has been conducted in order to consider more carefully the effects of transport properties on the process and product design.

When first approached, kinetic theory of gases can seem like a bewildering collection of isolated facts. With deep study, however, it becomes evident that there only a few fundamental concepts that underline all facts and events in kinetic theory [Chapman and Cowling, 1964; Hirschfelder et al., 1964]. Far from being a collection of isolated facts, kinetic theory is a well-organized logical subject unified by a few broad themes. When these themes are understood, learning kinetic theory becomes much easier [Kang and Sangani, 2002; Xiufeng and Xi, 1996; Barker et al., 1964; Vasserman and Khasilev, 1992; Amoros et al., 1992].

On the other hand, intermolecular forces are a fundamental ingredient for both equilibrium and transport properties such as calculation of partial molar volumes [Kwon et al., 2005], transport properties of simple fluids [Eskandari Nasrabad and Deiters, 2003; Eskandari Nasrabad et al., 2004; Xiufeng and Xi, 1996; Barker et al., 1964; Vasserman and Khasilev, 1992; Amoros and Maseo, 1992] and computer simulations [Laghaei et al., 2005a, b, 2006; Eskandari Nasrabad et al., 2005, 2006; Erpenbeck, 1983; Cumming and Evans, 1992; Maghari and Yeganegi, 2000a, b] of the fluid state. Knowledge of pair interactions between molecules is of great importance in the theory of fluids. Hence, the application of the theory of fluids to real substances relies on a knowledge of the interactions between real molecules [Trusler, 1991; Austin et al., 1984; Smith et al., 1985]. Various methods of determining intermolecular potentials have been used, either theoretical, based on experimental information, or combining both approaches fluids [Oh, 2004; Mourtis and Rummens, 1977]. Among these methods, inversion of dilute gas properties has been of particular importance [Vesovic and Wake-

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ham, 1987; Smith, 1987; Maitland et al., 1982, 1985a, b, 1986]. For the noble gases, which have spherically symmetric interactions, inversion of transport properties data is directly related to the pair interaction potential u(r). For near-spherical and non-spherical molecules inversion of transport properties gives an effective spherical potential $u_{eff}(r)$ related to, but different from, the true pair potential $u(r, \omega)$ which depends on the intermolecular orientation, ω [Haghighi et al., 2002].

In the present work, first the Wang Chang-Uhlenbeck-de Boer theory [Wang-Chang et al., 1964] has been applied to evaluate the various internal degrees of freedom to the thermal conductivity of N_2, O_2 and CO_2 at zero density. Then, the Rainwater-Friend theory [Bich and Vogel, 1996] has been applied to evaluate the thermal conductivity of oxygen and nitrogen in moderately-density regime at gaseous state. The theories are briefly re-explained in the following section.

KINETIC THEORY AND PAIR-INTERACTION INTERMOLECULAR POTENTIAL ENERGY FUNCTION

The intermolecular interaction between two spherical molecules (or atoms) in the gas phase can be characterized in terms of a pair potential energy function U(r) which describes the overall resultant (positive) repulsive energy between the molecules at small separations r, the resultant (negative) attractive energy at larger distances, and the asymptotic approach of the resultant attractive energy to zero at very large separations. Two characteristic features of this function [Rigby et al., 1984] are, first, the separation at which the interaction energy passes through zero, this distance being referred to as the collision diameter σ, and, second, the position of minimum interaction energy V, i.e., of greatest attraction. This position is referred to as the equilibrium separation r_m at which the interaction energy has a value $-\varepsilon$, where ε is termed the well depth. If U(r) is known, the various transport properties of the system may be calculated by rigorous kinetic theory, which uses equations involving collision integrals, $\Omega^{(l,s)}$, which are integrals over the full range of energies, trajectories of collision, and orientations of molecules during collisions. It should also be mentioned that the indices l, s specify weighting factors related to the mechanism of transport by molecular collisions. The Chapman-Enskog solution of the Boltzmann kinetic equation for dilute monatomic gases relates these coefficients to a series of collision integrals $\Omega^{(l,s)}$ [Chapman and Cowling, 1964]. The collision integrals, $\Omega^{(l,s)}$, are defined as [Hirschfelder et al., 1964]:

$$\Omega^{(l,s)} = [(s+1)!(kT)^{s+2}]^{-1} \int_0^\infty Q^{(l)}(E) e^{-E/kT} E^{s+1} dE \tag{1}$$

where E is the relative energy of colliding partners. The $Q^{(l)}(E)$ is a transport collision integral that classically is given by the equation [Hirschfelder et al., 1964],

$$Q^{(l)}(E) = 2\pi \{1 - [1 + (-1)^l/2(l+1)]\}^{-1} \int_0^\infty (1 - \cos^l \theta) b \, db \tag{2}$$

in which θ is the relative scattering angle between two colliding partners of energy E and impact parameter b at the gas temperature.

The scattering angle θ is calculated as a function of b and E from the following equation of motion,

$$\theta(b, E) = \pi - 2b \int_{r_0}^\infty [1 - b^2/r^2 - U(r)/E]^{-1/2} dr/r^2 \tag{3}$$

where the distance of closest approach r_0 is the outermost root of

$$1 - b^2/r_0^2 - U(r_0)/E = 0 \tag{4}$$

It is worth noting that three successive numerical integrations (i.e., Eq. (1)-(3)) are required to obtain the collision integral. Numerical differentiation and use of the recursion relation can generate collision integrals higher than that mentioned [Hirschfelder et al., 1964],

$$\Omega^{*(l,s+1)} = \Omega^{*(l,s)} \left[1 + \left(\frac{1}{s+2}\right)(d\ln\Omega^{*(l,s)}/d\ln T^*) \right] \tag{5}$$

where the reduced collision integral is defined by [Hirschfelder et al., 1964],

$$\Omega^{(l,s)*} = \Omega^{(l,s)}/\pi\sigma^2 \tag{6}$$

where σ is the length scaling factor such that $U(\sigma)=0$. The reduced temperature (T^*) is [Hirschfelder et al., 1964],

$$T^* = kT/\varepsilon \tag{7}$$

and ε is the energy scaling factor.

The kinetic theory expression for the thermal conductivity coefficient of a pure monatomic dilute gas of molecular mass, m, at the temperature, T, is [Hirschfelder et al., 1964]

$$\lambda(T) = \frac{75}{64\sigma^2} \frac{(k_B^3 T/\pi m)^{1/2}}{\Omega^{*(2,2)}} \tag{8}$$

Here k_B is the Boltzmann constant, $\Omega^{(2,2)*}$ is reduced thermal conductivity collision integral.

THERMAL CONDUCTIVITY

The subject of transport phenomena [Bird et al., 1960; Brush, 2003; Wakeham, 1992; McCourt, 1992] is a very old one, with some of topics dating back several centuries. Transport coefficients describe the process of relaxation to equilibrium from a state perturbed by application of temperature, pressure, density, velocity or composition gradients. The theoretical description of these phenomena constitutes a part of non-equilibrium statistical mechanics known as the kinetic theory. As mentioned in the previous section and with the related equations having been written, the ultimate purpose of this theory is to relate the macroscopic properties of the individual molecules and their interaction potentials. The kinetic theory of gases yields theoretical expressions for the viscosity, thermal conductivity and other transport coefficients [Choh and Uhlenbeck, 1958; Bogolubov, 1962; Cohen, 1965] for gases, the results of which are in reasonably good agreement with experiment. The kinetic theory treatment of transport properties in gases is grossly complicated from mathematical and physical viewpoints [Taxman, 1958]. The rigorous expressions underlying transport phenomena in gases were worked out in 1860 and 1870 by Maxwell and Boltzmann, but it was not until 1917 when Chapman and Enskog, working independently, solved the equations [Chapman and Cowling, 1964]. In general, the first improvement on the Enskog dense-gas theory must lie in avoiding the binary collision hypothesis, which would not be expected to hold in a dense fluid where higher-order collisions are

expected. Some attempts at dealing with this problem have been made by Choh and Uhlenbeck [1958], Cohen [1965] and Bogol-ubov [1962]. In general, these theories are based on density expansions for λ in terms of a series expansion in the density

$$\lambda = \lambda^{(0)}(1 + B_\lambda \rho + C_\lambda \rho^2 + \ldots) \qquad (9)$$

where the first term $\lambda^{(0)}$ is the dilute-gas transport coefficient and the second term from contributions from collision transfer and also from ternary collisions. The B_λ and C_λ are called the transport virial coefficients because of the analogy with the coefficients in the familiar virial expansion of the pressure. The aforesaid expansion in powers of the density is also called initial density dependence.

On the other hand, in the Wang Change-Uhlenbeck-de Boer (WCUB) version of the kinetic theory of gases [Wang-Chang et al., 1964], each molecular degree of freedom contributes separately to the thermal conductivity, and hence the thermal conductivity is written as a sum of contributions from translational, rotational, vibrational and electronic degrees of freedom:

$$\lambda^{(0)} = \lambda^{(0)}_{tr.} + \lambda^{(0)}_{rot.} + \lambda^{(0)}_{vib.} + \lambda^{(0)}_{ele.} \qquad (10)$$

To a first approximation these contributions are independent except for translational and rotational contributions which their interaction must be taken into account. Moreover, the translational contribution is like that of a monatomic gas and the other contributions correspond to the transport of molecular internal energy by a diffusion mechanism. That is, each internal degree of freedom is approximated by the mass diffusion coefficient, D. It should be mentioned that electronic energy rarely plays any role; it is therefore a reasonable approximation to take the electronic degrees of freedom as independent and to take $D_{elec} \approx D$. Also, it is a good approximation to take $D_{vib} \approx D$.

So the problem of prediction of thermal conductivity using WCUB theory reduces to the determination of the translational-rotation interaction and the diffusion coefficients for rotational energy. Translation-rotation interaction is denoted by ζ_{rot}, which is called rotational relaxation. Uribe and co-workers [Mason and Uribe, 1996] calculated the behavior of D_{rot} from ζ_{rot}.

The formulae needed for the calculation of λ are given below [Mason and Uribe, 1996]:

$$\frac{m\lambda^{(0)}_{vib.}}{\eta^{(0)}k_B} = \frac{6}{5}A^*\frac{C_{vib}}{k_B} \qquad (11)$$

$$\frac{m\lambda^{(0)}_{ele.}}{\eta^{(0)}k_B} = \frac{6}{5}A^*\frac{C_{elec}}{k_B} \qquad (12)$$

$$\frac{m\lambda^{(0)}_{tr.}}{\eta^{(0)}k_B} = \frac{5}{2}\left(\frac{3}{2} - \Delta_{rot}\right)(1 + \Delta_{spin}) \qquad (13)$$

$$\frac{m\lambda^{(0)}_{rot.}}{\eta^{(0)}k_B} = \frac{\rho D^{ex}_{rot}}{\eta^{(0)}}\left(\frac{C_{rot}}{k_B} + \Delta_{rot}\right)(1 + \Delta_{spin}) \qquad (14)$$

where A^* is the ratio of $\Omega^{(2,2)^*}$ to $\Omega^{(1,1)^*}$ and D^{ex}_{rot} is the diffusion coefficient for rotational energy with a correction for resonant exchange included. The correction terms Δ_{rot} and Δ_{spin} are

$$\Delta_{rot} = \frac{\frac{2}{\pi\zeta_{rot}}\frac{C_{rot}}{k_B}\left(\frac{5}{2} - \frac{\rho D_{rot}}{\eta^{(0)}}\right)}{1 + \frac{2}{\pi\zeta_{rot}}\left(\frac{5}{3}\frac{C_{rot}}{k_B} + \frac{\rho D_{rot}}{\eta^{(0)}}\right)} \qquad (15)$$

$$\Delta_{spin} = \frac{C_{spin}\left(\frac{5}{2} + \frac{C_{rot}}{k_B}\right)\frac{\rho D_{rot}}{\eta^{(0)}}}{\left(1 + \frac{8}{15\pi\zeta_{rot}}\frac{C_{rot}}{k_B}\right)\frac{\rho D_{rot}}{\eta^{(0)}} + \frac{3}{5}\frac{C_{rot}}{k_B}} \qquad (16)$$

The C_{vib} was estimated through the following equation obtained from the statistical mechanics [Mc Quarrie, 1973]:

$$C_{vib}/R = \sum_{j=1}^{k}(\Theta_{vj}/T)^2\frac{\exp(-\Theta_{vj}/T)}{[1 - \exp(-\Theta_{vj}/T)]^2} \qquad (17)$$

Here, the symbol Θ_{vj} identifies the characteristic vibrational temperature for the vibrational degree of freedom j [Mc Quarrie, 1973].

The temperature dependence of ζ_{rot} is given by [Mason and Uribe, 1996]:

$$\frac{\zeta^\infty_{rot}}{\zeta_{rot}} = 1 + \frac{\pi^{3/2}}{2(T^*)^{1/2}} + \left(2 + \frac{\pi^2}{4}\right)\frac{1}{T^*} + \frac{\pi^{3/2}}{(T^*)^{3/2}} \qquad (18)$$

The correlation for D_{rot} in terms of ζ_{rot} is given in two parts: a low-temperature part [Mason and Uribe, 1996], which switches to high temperature result of Sandler [Mason and Uribe, 1996] at a reduced crossover temperature T^*_{cross},

For $T^* \leq T^*_{cross}$

$$\frac{\rho D_{rot}}{\eta^{(0)}} = (\zeta_{rot}/(\zeta^\infty_{rot})^{3/4})(1.122 + 4.552/T^*) \qquad (19)$$

For $T^* \geq T^*_{cross}$

$$\frac{\rho D_{rot}}{\eta^{(0)}} = \frac{\rho D^{(0)}}{\eta^{(0)}}(1 + 0.27/\zeta_{rot} - 0.44/\zeta^2_{rot} - 0.90/\zeta^3_{rot}) \qquad (20)$$

The resonant energy exchange corrections to D_{rot} depend on the molecular dipole and quadrupole moments.

$$\frac{D_{rot}}{D^{ex}_{rot}} = 1 + \Delta^{\theta\theta}_{ex} + \Delta^{\mu\theta}_{ex} + \Delta^{\mu\mu}_{ex} \qquad (21)$$

$$\Delta^{\theta\theta}_{ex} = 1.31g^{\theta\theta}\left(\frac{7}{2}\pi^{3/2}\right)\Gamma\left(\frac{7}{4}\right)\left(\frac{\Theta^2}{\eta}\right)^{1/2}\left(\frac{kT}{m}\right)^{1/4} \times \frac{\rho D_{rot}}{k_B T}\left(\frac{\theta_{rot}}{T}\right)^{3/2} \qquad (22)$$

$$\Delta^{\mu\theta}_{ex} = 0.51g^{\mu\theta}\left(\frac{56}{45}\pi^2\right)^{1/3}\left(\frac{3}{5}\right)^{1/2}(\pi^2/6)^{1/3}\left(\frac{\mu\Theta}{\eta}\right)^{2/3}\left(\frac{k_B T}{m}\right)^{1/6}$$
$$\times \frac{\rho D_{rot}}{k_B T}\left(\frac{\theta_{rot}}{T}\right)^{3/2} \qquad (23)$$

$$\Delta^{\mu\mu}_{ex} = 0.44g^{\mu\mu}\left(\frac{3}{2}\pi^2\right)\left(\frac{\pi}{2}\right)^{1/2}\left(\frac{\mu^2}{\eta}\right)^{1/2} \times \frac{\eta^{(0)}}{k_B T}\left(\frac{\theta_{rot}}{T}\right)^{3/2} \qquad (24)$$

where Θ is the quadrupole and $\theta_{rot} = \eta^2/2kI$ is the characteristic rotational temperature, in which I is the molecular moment of inertia. The quantities $g^{\mu\theta}$, $g^{\mu\mu}$, $g^{\theta\theta}$ are dimensionless factors of order unity that correct for the replacement of quantum-mechanical summations by integrations. Its high-temperature asymptotic form is [Mason and Uribe, 1996]:

$$g^{\theta\theta} = \exp(-13\theta_{rot}/6T)[1 - (4\theta_{rot}/3T) + \ldots] \qquad (25)$$

$$g^{\mu\theta} = \exp(-17\theta_{rot}/12T)[1 - (5\theta_{rot}/6T) + \ldots] \qquad (26)$$

$$g^{\mu\mu} = \exp(-2\theta_{rot}/6T)[1 - (\theta_{rot}/3T) + \ldots] \qquad (27)$$

which are sufficiently accurate for most purposes. It should also be noted that in the aforesaid equations $\eta^{(0)}$ and $D^{(0)}$ are the viscosity

and self-diffusion coefficients at zero density, respectively. In the cases of nitrogen, oxygen and carbon dioxide there are only quadrupole moments which must be considered.

INVERSION TECHNIQUE

In the interest of brevity, only a brief description of the inversion technique will be given here. The inversion technique is initiated by estimating G_η, an inversion function, from an initial model potential such as the LJ(12-6). The inversion function is a function of the reduced temperature (T^*) alone. We have estimated this function using the LJ (12-6) model as the initial model. Given a set of reduced viscosity coefficient collision integrals, $\Omega^{(2,2)*}$ over a wide range of reduced temperature from *the extended law of corresponding states* [Bzowski et al., 1990] on the one hand, and estimating the G_η function from initial model potential LJ(12-6) on the other, it is possible to transform a pair of data ($\Omega^{(2,2)*}$, T^*) to V/ε versus r/σ on the potential energy curve using the essential equations of the INVERSION method. Now, we can marshal the essential steps of the INVERSION procedure.

For molecules which interact with an inverse power potential we can write:

$$U(r)=C_m/r^m \qquad (28)$$

where C_m is a constant having both positive and negative values, and r is inter-nuclear distance. It has been shown that for molecules that interact with an inverse power law there is a relation between temperature and r as below [Rigby et al., 1984]:

$$\Omega^{(2,2)}(T)=(C_m/kT)^{2/m}F(m) \qquad (29)$$

where F(m) is a constant. We define characteristic values of separation r, such that

$$r=(\Omega^{(2,2)}(T)/\pi)^{1/2} \qquad (30)$$

and noting that $U(r)=C_m/r^m$, and we obtain:

$$[r(T)]^2=(C_m/kT)^{2/m}F(m)=(U(r)/C_m)^{-2/m} \qquad (31)$$

thus

$$U(r)=(F_m)^{-m/2}kT \qquad (32)$$

and writing $F^{-m/2}$ as G we obtain

$$U(r)=G(m)/kT \qquad (33)$$

for inverse power potential functions, G is a numerical constant. For the sake of simplicity we use G instead of G_η in the latest expression. For realistic potentials it is found that G varies with temperature in complicated way, since the collisions have different energies and probe different parts of the potential function (which, in terms of the model, have different effective values of m). It is also found that the variation of G with temperature is very similar for all realistic potential functions [Rigby et al., 1984] and we may write $U(r)=G_0(T)/kT$, where $G_0(T)$ is calculated by using an approximate potential function $U_0(r)$ such as a LJ(12-6) potential. The details of the INVERSION procedure, which has been applied on the *Extended Principle of Corresponding States* [Bzowski et al., 1990], have been described in Fig. 1. The considerable practical success of the inversion procedure comes from universality of the inversion function G(T^*) among a whole class of potential functions possessing repulsive and attractive branches joined by a single minimum.

As mentioned in the previous paragraphs, it is clear that for the chosen values of distance, which have been obtained from the correlated values of $\Omega^{*(2,3)}_{corr.}$ by the corresponding states principle, the value of $V^*_n(r^*)$ does not change much regardless of the value of number of iterations chosen (n>2). The details of the inversion (iteration) steps are given in Fig. 1.
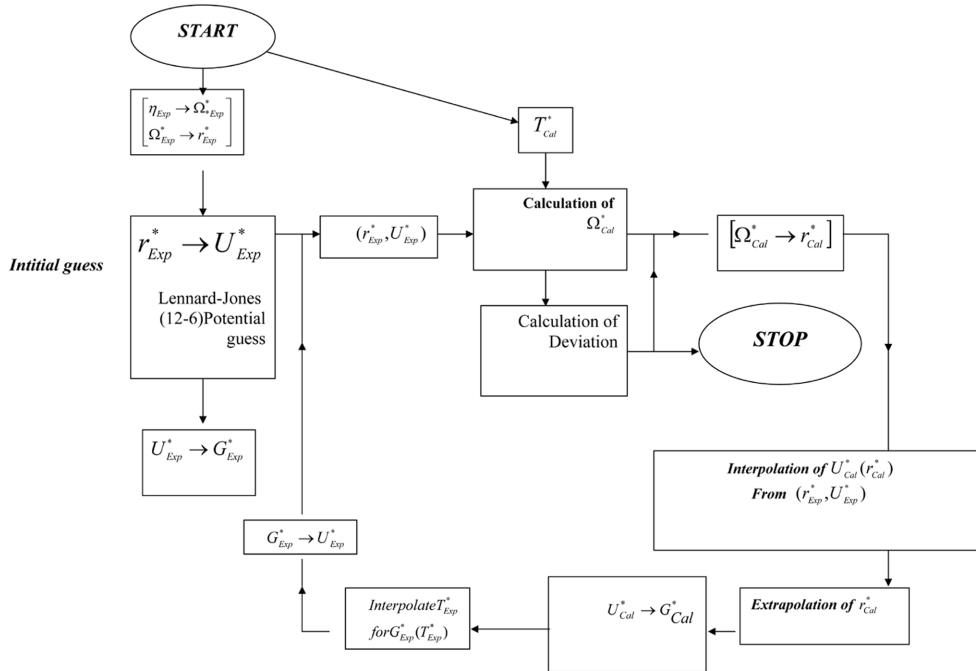

Fig. 1. Flow chart of the iteration steps in the inversion method.

In this work, the three consecutive integrals, Eqs. (2)-(4), are evaluated by using numerical integration [Clenshaw and Curtis, 1960] and the computer program developed by O'Hara and Smith [1970, 1971] and Neufeld and Aziz [1972]. It may also be pointed out that the integral of deflection angle, Eq. (3), is integrated by the trapezium rule [Buchnan and Turner, 1992; Conte and de Boor, 1980;

Table 1. The reduced collision integrals and their ratios for the N$_2$ system at zero density.

$$A^* \equiv \frac{\langle \Omega^{(2,2)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \; B^* \equiv \frac{5 \langle \Omega^{(1,2)*} \rangle - 4 \langle \Omega^{(1,3)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}, \; C^* \equiv \frac{\langle \Omega^{1,2*} \rangle}{\langle \Omega^{1,1*} \rangle}, \; E^* \equiv \frac{\langle \Omega^{(2,3)*} \rangle}{\langle \Omega^{(2,2)*} \rangle}, \; F^* \equiv \frac{\langle \Omega^{(3,3)*} \rangle}{\langle \Omega^{(1,1)*} \rangle}.$$

Log T*	$<\Omega^{*(1,1)}>$	$<\Omega^{*(2,2)}>$	A*	B*	C*	E*	F*
0.0	1.5810	1.4167	1.1159	1.2056	0.8421	0.8759	0.9188
0.1	1.4143	1.2746	1.1096	1.1735	0.8528	0.8832	0.9254
0.2	1.2768	1.1569	1.1036	1.1468	0.8671	0.8952	0.9350
0.3	1.1666	1.0610	1.0996	1.1269	0.8825	0.9090	0.9465
0.4	1.0797	0.9834	1.0980	1.1134	0.8973	0.9226	0.9584
0.5	1.0110	0.9202	1.0988	1.1054	0.9101	0.9344	0.9698
0.6	0.9560	0.8679	1.1015	1.1014	0.9204	0.9438	0.9799
0.7	0.9109	0.8238	1.1058	1.1007	0.9280	0.9509	0.9884
0.8	0.8728	0.7853	1.1114	1.1033	0.9332	0.9562	0.9949
0.9	0.8401	0.7507	1.1191	1.1103	0.9358	0.9605	0.9993
1.0	0.8112	0.7182	1.1294	1.1220	0.9358	0.9633	1.0026
1.1	0.7844	0.6865	1.1425	1.1360	0.9332	0.9631	1.0061
1.2	0.7568	0.6547	1.1560	1.1460	0.9291	0.9584	1.0117
1.3	0.7255	0.6225	1.1655	1.1456	0.9252	0.9495	1.0190
1.4	0.6893	0.5907	1.1669	1.1323	0.9239	0.9394	1.0263
1.5	0.6494	0.5609	1.1578	1.1086	0.9267	0.9318	1.0312
1.6	0.6089	0.5344	1.1394	1.0797	0.9339	0.9294	1.0325
1.7	0.5712	0.5123	1.1151	1.0512	0.9444	0.9331	1.0307
1.8	0.5392	0.4950	1.0891	1.0273	0.9566	0.9420	1.0270
1.9	0.5138	0.4825	1.0651	1.0096	0.9687	0.9538	1.0226
2.0	0.4953	0.4739	1.0450	0.9982	0.9793	0.9661	1.0186

Table 2. Same as Table 1 for O$_2$ system

Log T*	$<\Omega^{*(1,1)}>$	$<\Omega^{*(2,2)}>$	A*	B*	C*	E*	F*
0.0	1.5732	1.4100	1.1158	1.2048	0.8482	0.8796	0.9226
0.1	1.4119	1.2734	1.1087	1.1729	0.8577	0.8864	0.9280
0.2	1.2781	1.1592	1.1025	1.1463	0.8709	0.8979	0.9368
0.3	1.1705	1.0657	1.0984	1.1263	0.8855	0.9113	0.9478
0.4	1.0853	0.9895	1.0968	1.1125	0.8996	0.9242	0.9596
0.5	1.0175	0.9272	1.0973	1.1037	0.9120	0.9354	0.9709
0.6	0.9629	0.8757	1.0996	1.0989	0.9221	0.9444	0.9809
0.7	0.9179	0.8322	1.1030	1.0969	0.9299	0.9513	0.9893
0.8	0.8797	0.7944	1.1074	1.0974	0.9354	0.9563	0.9960
0.9	0.8465	0.7607	1.1128	1.1002	0.9389	0.9600	1.0011
1.0	0.8169	0.7297	1.1194	1.1052	0.9405	0.9624	1.0050
1.1	0.7894	0.7004	1.1270	1.1107	0.9405	0.9627	1.0089
1.2	0.7621	0.6720	1.1340	1.1132	0.9398	0.9604	1.0137
1.3	0.7332	0.6445	1.1377	1.1090	0.9394	0.9555	1.0197
1.4	0.7020	0.6183	1.1353	1.0966	0.9408	0.9499	1.0255
1.5	0.6690	0.5942	1.1258	1.0776	0.9448	0.9460	1.0295
1.6	0.6362	0.5732	1.1099	1.0557	0.9516	0.9456	1.0307
1.7	0.6060	0.5560	1.0900	1.0348	0.9602	0.9494	1.0291
1.8	0.5802	0.5427	1.0692	1.0176	0.9696	0.9566	1.0256
1.9	0.5598	0.5330	1.0501	1.0050	0.9785	0.9657	1.0213
2.0	0.5447	0.5266	1.0343	0.9968	0.9863	0.9750	1.0173

Table 3. Same as Table 1 for CO₂ system

Log T^*	$<\Omega^{*(1,1)}>$	$<\Omega^{*(2,2)}>$	A^*	B^*	C^*	E^*	F^*
0.0	1.4141	1.5798	1.1172	1.2088	0.8511	0.8815	0.9245
0.1	1.2789	1.4198	1.1102	1.1779	0.8590	0.8877	0.9283
0.2	1.1647	1.2866	1.1046	1.1521	0.8708	0.8988	0.9360
0.3	1.0702	1.1790	1.1016	1.1327	0.8842	0.9116	0.9467
0.4	0.9924	1.0929	1.1012	1.1187	0.8974	0.9236	0.9589
0.5	0.9284	1.0234	1.1023	1.1085	0.9093	0.9334	0.9712
0.6	0.8752	0.9660	1.1038	1.1005	0.9196	0.9409	0.9824
0.7	0.8304	0.9174	1.1047	1.0937	0.9282	0.9467	0.9918
0.8	0.7923	0.8755	1.1050	1.0886	0.9354	0.9516	0.9988
0.9	0.7593	0.8392	1.1053	1.0864	0.9411	0.9565	1.0033
1.0	0.7301	0.8081	1.1069	1.0882	0.9450	0.9614	1.0058
1.1	0.7034	0.7813	1.1108	1.0931	0.9470	0.9649	1.0077
1.2	0.6782	0.7569	1.1159	1.0971	0.9474	0.9654	1.0110
1.3	0.6540	0.7323	1.1197	1.0956	0.9474	0.9624	1.0162
1.4	0.6308	0.7058	1.1188	1.0861	0.9485	0.9576	1.0219
1.5	0.6094	0.6774	1.1116	1.0699	0.9518	0.9536	1.0264
1.6	0.5905	0.6486	1.0984	1.0507	0.9574	0.9526	1.0281
1.7	0.5748	0.6215	1.0813	1.0321	0.9649	0.9553	1.0270
1.8	0.5626	0.5980	1.0630	1.0165	0.9730	0.9613	1.0239
1.9	0.5537	0.5791	1.0458	1.0051	0.9808	0.9691	1.0200
2.0	0.5477	0.5650	1.0315	0.9976	0.9877	0.9773	1.0161

Dorn and Mc Cracken, 1972]. The cross-section, Eq. (2), and the collision integrals, Eq. (1), are evaluated by using a Gauss-Legendre quadratrue (numerical integration) [Press et al., 1994; Smith, 1995; Hornbeck, 1975; Pachmer, 1984].

In the present work, we obtained accurate reduced potential energies for nitrogen and oxygen at low density by direct inversion of the viscosity collision integral equation. The collision integrals and their ratios are given in Tables 1-3.

RESULTS AND DISCUSSION

As mentioned before, the problem of obtaining the interaction potential energy is the extraction of information about the force by analyzing the bulk properties. The degree of success will depend on the accuracy of both the measurements and theory connecting the force to macroscopic properties, and on the sensitivity of this connection. The transport coefficients of dilute gases, especially viscosity, which depends on binary interaction, satisfy the above condition. It is worth noting that the terms "dilute" or "low-density" gas represent a real physical situation, whereas the frequently-used expression zero-density limit is related to results of a mathematical extrapolation of a density series of a particular transport property at constant temperature to zero density. The derived value is assumed to be identical with the true value for the dilute-gas state, a statement that in most cases turns out to be correct. In this respect, the inversion procedure plays an important role for generating a like-molecule potential from the viscosity data and their corresponding states correlation. This, in turn, permits us to calculate collision integrals, and, consequently, the transport properties more accurately than is possible by correlations of the corresponding states. In the case of the corresponding states principle, it must be mentioned that

since the functional equation obtained from this principle applies in a more limited form to molecular gases than to noble gases, the a-rithmetic mean of the functions should be used for the components of gas mixtures. Also, we are confined only to $T^* \geq 1.0$, because viscosity collision integrals for molecular gases at low temperatures do not exist; consequently, in order to proceed to the next iteration it is necessary to extrapolate V(r) in the long-range region (low temperature). The extrapolation function that we have used is $V^* = -C_6 u^6$, where C_6 is the dispersion coefficient and u is the reciprocal of the intermolecular distances, both in atomic units. It is remarkable that the inversion procedure is not unduly sensitive to the nature of the extrapolating function. Regarding the aforesaid discussion and existence of corresponding states viscosity coefficients at high temperatures (repulsive region), the inversion was established. It should be mentioned that although we used just $V^* = -C_6 u^6$ as the extrapolating function at long range region, the inversion function procedure is not unduly sensitive to the nature of the used extrapolating functions. This is due to the fact that the potential will adjust itself during iteration steps (as depicted in the flow chart). As mentioned before, the inversion function $G_\eta(T^*)$ is found to be remarkably insensitive to the precise nature of the potential, a feature which greatly enhances the convergence rate of the inversion. It is worthwhile to note that for a given transport property, $G_\eta(T^*)$ is determined by the ratio of the impact parameter to the distance of closest approach for a collision at an energy $\cong (s+1)kT$, which results in a deflection angle of $\theta \sim \pi^{-1}$ [Maitland et al., 1985b]. It is remarkable that in s has its usual meaning, which was pointed out in the previous section 2 (§ Kinetic Theory and Pair-Interaction Intermolecular Potential Energy Function). Maintaining this deflection angle constant as the potential changes requires the impact parameter to be changed. The distance of closest approach will change in the same direction and by roughly

the same magnitude; due to this small deflection angle, the impact parameter and the distance of closest approach are similar. One therefore expects their ratios, and hence the $G_\eta(T^*)$ function (and consequently extrapolated function), to be essentially independent of the precise nature of the potential.

Based upon the aforesaid paragraph, a conclusion central to our study is that it seems to describe an interesting application of the inversion method as a universal form. Hence, toward the eventual goal of a fundamental and unambiguous methodology of the inversion procedure, the objective of the present paper is universality of the application of inversion method.

The accuracies of the calculated transport properties arise from the intermolecular potential energy obtained from the inversion procedure. In the present study, the direct inversion procedure was applied to corresponding states of viscosity given by Bzowski et al. [1990] to generate a unique spherically effective pair potential energies, which we claim are reliable. This claim is based on these facts that the revision of the extended principle of the corresponding states by Bzowski et al. [1990] correlates the viscosity of the molecules and their mixtures at low density over a very wide temperature range with very good accuracies and characterizes each binary interaction with the aid five classical-material parameters σ, ε, ρ^*, C_6^*, and V_0^* [Najafi et al., 1983].

It should be mentioned that the vibrational frequencies necessary for calculating the vibrational part of the thermal conductivity were taken from McQuarrie [1973]. It should also be pointed out that the contribution to λ_{elec} is small because the corresponding contributions to the heat capacity are small for the range of temperatures considered here. Henceforth, in the present calculations, we neglected the term λ_{elec}.

Terms $\Delta_{ex}^{\mu\theta}$ and $\Delta_{ex}^{\mu\mu}$ are zero for nitrogen and oxygen molecules because they have no dipole moment. Therefore, for a given temperature, the first step is the calculation of ζ_{rot} and D_{rot} from Eqs. (18) and (19) or (20). D_{rot} can be used to calculate D_{rot}^{ex} via Eqs. (21)-(27). From ζ_{rot} and D_{rot}, Δ_{rot} and Δ_{spin} are calculated by the use of Eqs. (15) and (16). Applying D_{rot}^{ex} and Δ_{rot} values to Eqs. (11)-(14), the thermal conductivity λ can computed. The viscosity coefficient η and self-diffusion coefficient D at zero density needed in the calculation of the thermal conductivity coefficient were taken from the present calculations. After calculating the various contributions to the thermal conductivity at the zero density due to internal degree of freedom then, we calculated the thermal conductivity
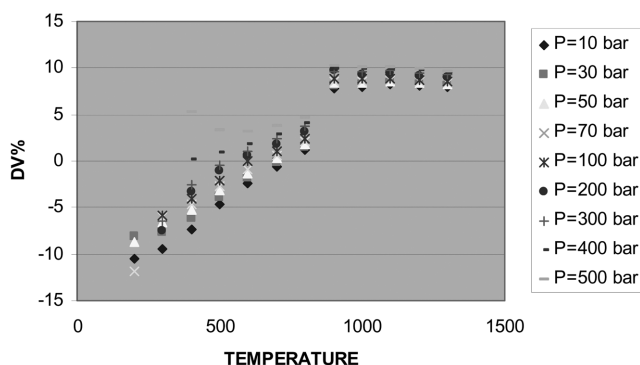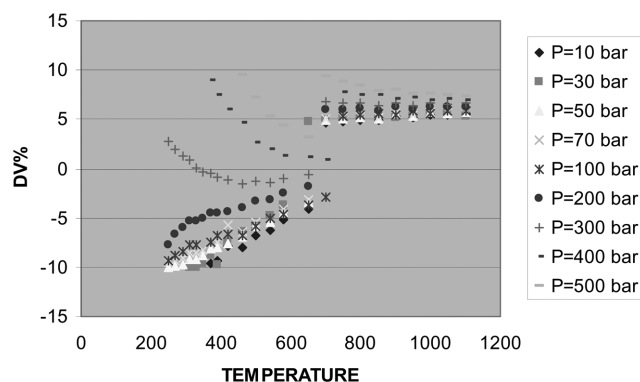

Fig. 3. Deviation values of thermal conductivity for N_2. The experimental values are adopted from Stephan et al. [1987].
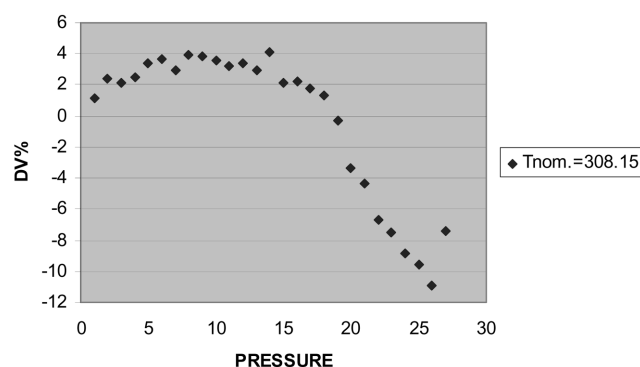

Fig. 4. Deviation values of thermal conductivity for CO_2. The experimental values are adopted from Millat et al. [1987].

at moderate density by the correlation which has been proposed by Najafi et al. [Ghayeb, 2003, 2004].

Deviation plots for thermal conductivity coefficients of O_2, N_2 and CO_2 systems are shown in Figs. 2-4.

CONCLUSIONS

We have used the reasonably effective potential energy function to obtain improved collision integrals needed for the calculation of the transport properties. The main advantage of the ratios of the collision integrals obtained from the inversion of the corresponding states of viscosity is that it is more accurate than those obtained from other corresponding states because measurements of viscosity are more practical than those of other transport properties.

The calculation of thermal conductivity from the INVERTED potential by means of WCUB approach, and subsequent comparison with the experimentally based values, has been shown to provide a powerful test of the accuracy of the INVERTED potential. It is an advancement over the traditional approaches that consider a potential function with several parameters and try to adjust them using experimental results. This scheme provides an accurate potential energy and allows determination of collision integrals more accurately than is possible by the extended law of corresponding states. The direct inversion of the viscosity collision integral correlation obtained from an extended law of corresponding states is obviously a powerful method for establishing an accurate unlike-pair

Fig. 2. Deviation values of thermal conductivity for O_2. The experimental values are adopted from Laesecke et al. [1990].

potential energy. The accurate potential energy obtained by inversion of viscosity data can reproduce (within precision of the experimental data) all transport properties. Our estimated accuracy is within 10% for thermal conductivity.

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NOMENCLATURE

b   : impact parameter
l, s   : specify weighting factors related to the mechanism of transport by molecular collisions
r   : intermolecular distance
k   : Boltzmann constant
m   : molecular mass
u   : reciprocal of the intermolecular distance
C_6 : dispersion coefficient
E   : relative kinetic energy
G   : inversion function
T   : absolute temperature
V(r)   : intermolecular potential energy
A^*, B^*, C^*, E^*, F^* : ratios of collision integral
T^* : reduced temperature
$Q^{(l)}(E)$: transport collision integral
$D^{(0)}$: self-diffusion coefficient at zero density
D_{rot} : coefficient for diffusion of molecular rotational energy
D_{vib} : coefficient for diffusion of molecular vibrational energy
D_{elec} : coefficient for diffusion of molecular electronic energy
D_{rot}^{ex} : diffusion coefficient for rotational energy including correction for resonant exchange
C_{vib} : molar heat capacity due to molecular vibration
C_{rot} : molar heat capacity due to molecular rotation
C_{elec} : molar heat capacity due to molecular electronic degrees of freedom
B_λ : transport virial coefficient
C_λ : transport virial coefficient
$g^{\mu\mu}$: temperature-dependent dimensionless factor needed in calculation of $\Delta_{ex}^{\mu\mu}$
$g^{\mu\theta}$: temperature-dependent dimensionless factor needed in calculation of $\Delta_{ex}^{\mu\theta}$
$g^{\theta\theta}$: temperature-dependent dimensionless factor needed in calculation of $\Delta_{ex}^{\theta\theta}$

Greek Letters

ε : energy scaling factor
σ : length scaling factor
θ : relative scattering angle between two colliding partners
$\Omega^{(l,s)}$: collision integral
$\Omega^{(l,s)*}$: reduced collision integral
$\Omega^{(1,1)*}$: reduced collision integral for diffusion
$\Omega^{(2,2)*}$: reduced collision integral for viscosity (or thermal conduc-

tivity)
$\eta^{(0)}$: viscosity coefficient at zero density
$\lambda^{(0)}$: thermal conductivity at zero density
$\lambda_{tr.}^{(0)}$: contribution of molecular translational energy to thermal conductivity at zero density
$\lambda_{rot.}^{(0)}$: contribution of molecular rotational energy to thermal conductivity at zero density
$\lambda_{vib.}^{(0)}$: contribution of molecular vibrational energy to thermal conductivity at zero density
$\lambda_{ele.}^{(0)}$: contribution of molecular electronic energy to thermal conductivity at zero density
$\Delta_{ex}^{\mu\theta}$: correction for resonant exchange of molecular rotational energy due to dipole-quadrupole interactions
$\Delta_{ex}^{\theta\theta}$: correction for resonant exchange of molecular rotational energy due to quadrupole-quadrupole interactions
$\Delta_{ex}^{\mu\mu}$: correction for resonant exchange of molecular rotational energy due to dipole-dipole interactions
ζ_{rot} : collision number for rotational relaxation
ζ_{rot}^∞ : high-temperature asymptotic value of collision number for rotational relaxation
Δ_{rot} : correction to λ for interaction of molecular rotational and translational energy
Δ_{spin} : correction to λ for alignment of molecular angular momentum (spin polarization)
Θ : quadrupole moment
$\theta_{rot}= \eta^2/2kI$: characteristic rotational temperature
θ_{vj} : characteristic vibrational temperature
ρ : mass density of gas

Subscripts
Exp. : experimental
Corr. : corresponding states
Calc. : calculated

REFERENCES

An, J. and Kim, H., "A simplified expression for the hard sphere dimer fluid radial distribution function," *Korean J. Chem. Eng.*, **22**, 103 (2005).

Amoros, A., Maseo, M. J. and Villar, E., "A test of the modified Enskog theory for the transport properties of liquids," *Int. J. Thermophys.*, **13**, 907 (1992).

Austin, J. W., Dominick, P., Smith, E. B., Tindell, A. R. and Wells, B. H., "Effective spherical potentials for molecular fluids," *Mol. Phys.*, **52**, 1393 (1984).

Bae, S. Y., Cho, D.-H. T., Kim, H. T. and Kumazawa, H., "Transport of oxygen and carbon dioxide phenomena through polycarbonates membranes," *Korean J. Chem. Eng.*, **11**, 127 (1994).

Bae, S. Y., Kim, H. T. and Kumazawa, H., "Transport phenomena in gas permeation trough glassy polymer membranes with concentration-dependent sorption and diffusion parameters," *Korean J. Chem. Eng.*, **11**, 211 (1994).

Barker, J. A., Fock, W. and Smith, F., "Calculation of gas transport properties and the interaction of argon atoms," *Phys. Fluids*, **7**, 897 (1964).

Bich, E. and Vogel, E., "Initial density dependence of transport properties" in *Transport Properties of Fluids (Their Correlation, Prediction and Estimations)*, Edited by J. Millat, J. H. Dymond and C. A.

Nieto de Castro, Cambridge University Press, Cambridge, Sec. 5.2, 72 (1996).

Bird, B. R., Stewart, W. E. and Lightfoot, E. N., *Transport phenomena*, Wiley International Edition, New York, Chapter 8 (1960).

Boushehri, A., Bzowski, J., Kestin, J. and Mason, E. A., "Equilibrium and transport properties of eleven polyatomic gases at low density," *J. Phys. Chem. Ref. Data*, **16**, 445 (1987).

Bogolubov, G. N. N., in *Studies in statistical mechanics*, vol. 7, Edited by J. de Boer and G. E. Uhlenbeck, North-Holland, Amsterdam, 5 (1962).

Brush, S. G., *The kinetic theory of gases*, Vol. 1, Imperial College Press, Oxford (2003).

Buchnan, J. L. and Turner, P. R., *Numerical methods and analysis*, McGraw-Hill, New York, 471 (1992).

Bzowski, J., Kestin, J., Mason, E. A. and Uribe, F. J., "Equilibrium and transport properties of gas mixture at low density: Eleven polyatomic gases and five noble gases," *J. Phys. Chem. Ref. Data*, **19**, 1179 (1990).

Choh, S. T. and Uhlenbeck, G. E., *The kinetic theory of phenomena in dense gases*, University of Michigan, Michigan (1958).

Clenshaw, C. W. and Curtis, A. R., "A method for numerical integration on an automatic computer," *Numerische Mathematik*, **2**, 197 (1960).

Conte, S. D. and de Boor, C., *Elementary numerical analysis*, third Edition, Mc Graw Hill, New York, 303 (1980).

Cohen, E. G. D., in *Statistical mechanics of equilibrium and non-equilibrium processes*, Edited by J. Meixner, North-Holland, Amsterdam, 140 (1965).

Cumming, P. T. and Evans, D. J., "Non-equilibrium molecular dynamics approaches to the transport properties and non-newtonian fluid rheology," *Ind. Eng. Chem. Res.*, **31**, 1237 (1992).

Dorn, W. S. and Mc Cracken, D. D., *Numerical methods with fortran IV case studies*, John-Wiley, New York, 244 (1972).

Eskandari Nasrabad, A. and Deiters, U. K., "Prediction of thermodynamic properties of krypton by Monte Carlo simulation using ab initio potentials," *J. Chem. Phys.*, **119**, 947 (2003).

Eskandari Nasrabad, A., Laghaei, R. and Deiters, U. K., "Prediction of thermophysical properties of pure neon, argon, and the binary mixtures neon-argon and argon-krypton by Monte Carlo simulation using ab initio potentials," *J. Chem. Phys.*, **121**, 6423 (2004).

Eskandari Nasrabad, A., Laghaei, R. and Eu, B. C., "Modified free volume theory of self-diffusion and molecular theory of shear viscosity of liquid carbon dioxide," *J. Phys. Chem. B*, **109**, 8171 (2005).

Eskandari Nasrabad, A., Laghaei, R. and Eu, B. C., "Molecular theory of thermal conductivity of the lannard-jones fluid," *J. Chem. Phys.*, **124**, 84506 (2006).

Erpenbeck, J. J., "Non-equilibrium molecular dynamics calculations of the shear viscosity of hard spheres," *Physica*, **118A**, 144 (1983).

Ghayeb, Y., Najafi, B., Moeini, V. and Parsafar, G. A., "Viscosity calculation of supercritical gases based on the modified Enskog theory," *High Temp.-High Press.*, **35/36**, 217 (2003/2004).

Haghighi, B., Fathabadi, M. and Papari, M. M., "Semi-empirical calculation of the transport properties of N_2-noble gases mixtures at low density by the inversion method," *Fluid Phase Equil.*, **203**, 205 (2002).

Hill, T. L., *An introduction to statistical thermodynamics*, Wiley, New York (1960).

Hill, T. L., *Thermodynamics of small systems*, Wiley, New York (1960).

Hirschfelder, J. O., Curtis, C. F. and Bird, R. B., *Molecular theory of gases and liquids*, John-Wiley, New York, Chapter 7 (1964).

Hornbeck, R. W., *Numerical methods*, Prentice-Hall, New Jersey, 293 (1975).

Hussaindokht, M. R., Haghighi, B. and Bozorgmehr, M. R., "A comparison among three equation of state in predicting the solubility of some solids in super critical carbon dioxide," *Korean J. Chem. Eng.*, (2006) Accepted for publication.

Jang, J. G., Park, H. B. and Lee, Y. M., "Molecular thermodynamic approach on phase equilibria of dendritic polymer systems," *Korean J. Chem. Eng.*, **20**, 386 (2003).

Kang, S. P., Lee, H., Lee, Y.-W. and Lee, Y. -Y., "Correlation of the vapor-liquid equilibria of CFC, HCFC and FC mixtures: Critical evaluation of mixing rules," *Korean J. Chem. Eng.*, **12**, 535 (1995).

Kang, S.-Y. and Sangani, A. A., "Numerical simulations and kinetic theory of bubbly liquids rheology under microgravity," *Korean J. Chem. Eng.*, **19**, 363 (2002).

Kirkwood, J. G. and Oppenheim, I., *Chemical thermodynamics*, Wiley, New York (1960).

Kwon, Y. J., Lee, J. Y. and Kim, K. C., "Application of the Kirkwood-Buff solution formalism and the hard sphere expansion method with the modified mean density approximation to predict solubility of solutes in supercritical fluids," *Korean J. Chem. Eng.*, **14**, 184 (1997).

Kwon, Y. J. and Lee, W., "Prediction of infinite-dilution partial molar volumes of organic solutes in carbon dioxide using the Kirkwood-Buff fluctuation integral with hard sphere expansion (HSE) theory," *Korean J. Chem. Eng.*, **22**, 452 (2005).

Neufeld, P. D. and Aziz, R. A., "Program ACQN to calculate transport collision integrals adapted to run on IBM computers," *Comput. Phys. Commun.*, **3**, 269 (1972).

Laesecke, A., Krauss, R., Stephan, K. and Wagner, W., "Transport properties of fluid oxygen," *J. Phys. Chem. Ref. Data*, **19**, 1089 (1990).

Laghaei, R., Eskandari Nasrabad, A. and Eu, B. C., "Generic van der Waals equation of state: Modified free volume theory of diffusion, and viscosity of simple liquids," *J. Phys. Chem. B*, **109**, 5873 (2005a).

Laghaei, R., Eskandari Nasrabad, A. and Eu, B. C., "Pair correlation functions and the self-diffusion coefficient of Lennard-Jones liquid in the modified free volume theory of diffusion," *J. Phys. Chem. B*, **109**, 21375 (2005b).

Laghaei, R., Eskandari Nasrabad, A. and Eu, B. C., "Statistical mechanical theory of rheology: Lennard-Jones fluids," *J. Chem. Phys.*, **123**, 234507 (2005c).

Laghaei, R. Eskandari Nasrabad, A. and Eu, B. C., "Excluded volume in the generic van der Waals equation of state and the self-diffusion coefficient of the Lennard-Jones fluid," *J. Chem. Phys.*, **124**, 154502 (2006).

Maghari, A. and Yeganegi, S., "Non-equilibrium molecular dynamics study of thermal diffusion behavior of the MMSV potential model for hydrogen," *J. Phys. Soc. Jpn.*, **70**, 3261 (2000).

Maghari, A. and Yeganegi, S., "On the sensitivity of thermal diffusion to the intermolecular pair potential," *J. Phys. Soc. Jpn.*, **69**, 1389 (2000).

Mason, E. A. and Uribe, F. J., "The corresponding-states principle: Dilute gases," in *Transport Properties of Fluids (Their Prediction, Estimation and Correlations)*, Edited by Millat J., Dymond J. H., Nieto de Castro C. A., Cambridge University Press, Cambridge, 250 (1996).

Mc Quarrie, D. A., *Statistical mechanics*, Harper & Row, New York (1973).

Maitland, G. C., Vesovic, V. and Wakeham, W. A., "The effect of non-spherical interactions upon the transport properties of dilute polyatomic gases," *8ᵗʰ Proc. Symp. Thermophys. Prop.*, (1), 184 (1982).

Maitland, G. C., Vesovic, V. and Wakeham, W. A., "The inversion of thermophysical properties II. Non-spherical systems explored," *Mol. Phys.*, **54**, 301 (1985b).

Maitland, G. C., Mustafa, M., Vesovic, V. and Wakeham, W. A., "The inversion of thermophysical properties III. Highly anisotropic interactions," *Mol. Phys.*, **57**, 1015 (1986).

McCourt, F. R. W., "Status of kinetic theory," in *Status and Future Developments in the Study of Transport Properties*, W. A. Wakeham, A. S. Dickinson, F. R. W. McCourt, V. Vesovic (Eds.), NATO ASI, Kluwer, New York, 117 (1992).

Millat, J., Mustafa, M., Ross, M., Wakeham, W. A. and Zalaf, M., "The thermal conductivity of argon, carbon dioxide and nitrous oxide," *Physica A*, **145**, 461 (1987).

Monchick, L. and Mason, E. A., "Transport properties of polar gases," *J. Chem. Phys.*, **35**, 1676 (1961).

Mourtis, F. M. and Rummens, F. H. A., "A critical evaluation of Lennard-Jones and Stockmayer potential parameters and of some correlation methods," *Can. J. Chem.*, **55**, 3007 (1977).

Chapman, S. and Cowling, T. G., *The mathematical theory of non-uniform gases*, Third Edition, Cambridge University Press, Cambridge (1964).

Najafi, B., Mason, E. A. and Kestin, J., "Improved corresponding states principle for the noble gases," *Physica*, **119A**, 387 (1983).

O'Hara, H. and Smith, F. J., "The efficient calculation of the transport properties of dilute gas to a prescribed accuracy," *J. Comput. Phys.*, **5**, 328 (1970).

O'Hara, H. and Smith, F. J., "Transport collision integrals for a dilute gas," *Comput. Phys. Commun.*, **2**, 47 (1971).

Oh, S. K. and Sim, C. H., "An extension of the group contribution model for estimating and thermodynamic and transport properties of dilute gases," *Korean J. Chem. Eng.*, **19**, 843 (2002).

Oh, S. K. and Park, K. H., "An extension of the group contribution model for estimating and thermodynamic and transport properties, part II," *Korean J. Chem. Eng.*, **22**, 268 (2005).

Oh, S. K., "An extension of the group contribution model for estimating and thermodynamic and transport properties, part III," *Korean J. Chem. Eng.*, **22**, 949 (2005).

Oh, E. S., "van der Waals interaction energies between non-polar bodies," *Korean J. Chem. Eng.*, **21**, 493 (2004).

Pachmer, J., *Handbook of numerical analysis in application*, Mc Graw Hill, New York, pp. 140-142 and pp. 136-137 (1984).

Press, W. H., Teukolsky, S. A., Vetterling, W. T. and Flannery, B. P., *Numerical recipes in FORTRAN: The art of scientific computing*, Second Edition, Cambridge University Press, Cambridge (1994).

Rigby, M., Smith, E. B., Wakeham, W. A. and Maitland, G. C., *The forces between molecules*, Clarendon, Oxford (1992).

Shing, G. S., Park, J. S. and Kwon, Y. J., "An improved conformal solution method based on the hard sphere expansion to predict vapor-liquid equilibrium," *Korean J. Chem. Eng.*, **15**, 603 (1998).

Smith, I. M., *Programming in FORTRAN 90: A first course for engineers and scientists*, John-Wiley (1995).

Smith, E. B., "The determination of intermolecular forces by data-inversion methods," in *Structure and dynamic of weakly bonded molecular complexes, NATO ASI Series, Ser. C*, **212**, Kluwer, New York, 373 (1987).

Smith, E. B., Tindell, A. R. and Wells, B. H., "The determination of intermolecular forces between polyatomic molecules by the inversion of thermophysical properties," *High Temp.-High Press.*, **17**, 53 (1985).

Stephan, K., Krauss, R. and Laesecke, A., "Viscosity and thermal conductivity of nitrogen for a wide range of fluid states," *J. Phys. Chem. Ref. Data*, **16**, 993 (1987).

Taxman, N., "Classical theory of transport phenomena in dilute polyatomic gases," *Phys. Rev.*, **110**, 1235 (1958).

Tolman, R. C., *The principles of statistical mechanics*, Dover edition, New York (1979).

Maitland, G. C., Vesovic, V. and Wakeham, W. A., "The inversion of thermophysical properties I. Spherical systems revisited," *Mol. Phys.*, **54**, 287 (1985a).

Trusler, J. P. M., "Thermophysical properties and intermolecular forces in gases," *Sci. Prog.*, **75**, 51 (1991).

Vasserman, A. A. and Khasilev, P. I., "Calculation of the transport properties of dense fluids by means of a real intermolecular potential and the Enskog theory," *High Temp.-High Press.*, **24**, 475 (1992).

Vesovic, V. and Wakeham, W. A., "An interpretation of intermolecular pair potentials obtained by inversion for non-spherical systems," *Mol. Phys.*, **62**, 1239 (1987).

Wakeham, W. A., "Traditional transport properties," in *Status and Future Developments in the Study of Transport Properties*, W. A. Wakeham, A. S. Dickinson, F. R. W. McCourt, V. Vesovic (Eds.), NATO ASI, Kluwer, New York, 29 (1992).

Wang Chang, C. S., Uhlenbeck, G. E. and de Boer, J., "The heat conductivity and viscosity of polyatomic gases," in *Studies in statistical mechanics*, Edited by J. de Boer and G. E. Uhlenbeck, vol. 2, North-Holland, Amsterdam (1964).

Wang Chang, C. S., Uhlenbeck, G. E. and de Boer, J., "The heat conductivity and viscosity of polyatomic gases," in *Studies in Statistical mechanics*, Edited by J. de Boer and G. E. Uhlenbeck, vol. 2, North-Holland, Amsterdam (1964).

Xiufeng, L. and Xi, L., "Theoretical calculation of transport properties of the noble gases He and Ne and their binary mixtures at low density," *Int. J. Theor. Phys.*, **35**, 1753 (1996).

Yoo, K.-P., Kim, H. and Lee, C. L., "Unified equation of state based on the lattice fluid theory for phase equilibria of complex mixtures, part I. Molecular thermodynamic framework," *Korean J. Chem. Eng.*, **12**, 277 (1995).

Yoo, K.-P., Kim, H. and Lee, C. L., "Unified equation of state based on the lattice fluid theory for phase equilibria of complex mixtures, part II. Application to complex mixtures," *Korean J. Chem. Eng.*, **12**, 289 (1995).